“ **Novel Preparation and Magneto Chemical Characterization of Nano-Particle Mixed Alcohol Catalysts**”, Seetala V. Naidu, Upali Siriwardane, and Akundi N. Murty,
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Abstract

We have prepared Cu, Co, Fe, Cu/Co, Cu/Fe and Co/Fe on alumina-supported catalysts using sol-gel/oil-drop methods. Synthesis was carried out using both aluminum tri-sec-butoxide (ALTSB) and aluminum tri-iso-propoxide (ALTIP), and compared. The optimum calcination temperatures were studied by differential thermal analysis (DTA) and found to be below 450 ºC. We have developed methodologies for screening promising catalysts using a gas phase flow reactor connected to GC. We have used several other columns attached to GC to analyze compounds such as hydrocarbons and alcohols and measured their concentrations. We have used a slurry phase reactor to obtain kinetic data for the promising catalysts.

The particle size and metal loading of granules were studies by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis. The metal loading results were used to optimize the synthesis to obtain consistent metal compositions. The catalysts were investigated by powder X-ray diffraction (PXRD) and the results showed nano-particle nature of the metal oxides. We have modified sol-gel method to prepare nano-particle catalyst using commercially available nano-particles FeO and CuO, and to disperse them in alumina sol. We have compared the CO/H_2 conversion of sol-gel prepared nano-particle catalysts: 1) metal solution derived and 2) commercial nano-particle-oxides incorporated. Both types of these nano-particle catalysts showed comparable and higher conversion rates than the conventional catalysts prepared by co-precipitation methods.

We modified sol-gel method to thin film deposit metal nano-particles on micro reactors and studied the CO/H_2 conversions at micro scale and investigated feasibility of using micro reactors in catalyst screening. The CO/H_2 conversion of a micro-reactor coated with a sol-gel metal thin film has been compared with Co and Fe sputter coated reactors using GC/MS analysis of products.

We have modified sol-gel method for large-scale preparation of promising Co/Fe nano-particle catalysts. Comparative study of the ferromagnetic component of Co/Fe reduced and post-reaction catalysts were undertaken using a vibrating sample magnetometer (VSM). The magnetic results gave information on the reduction efficiency and the changes in metal centers during catalytic reactions. Catalyst with mixed metal Co/Fe compositions at 12% (prepared by sol-gel/oil- drop and metal solutions) showed the best conversion rates for the syngas conversion. Based on VSM results, Co is easily reduced and does not get deactivated compared to Fe. In mixed metal Co/Fe composition Co has higher metal loading than Fe, which could be explained in terms of solubility of metal hydroxides formed during sol-gel preparation. The mixed metal catalysts showed higher syngas conversion compared to the pure metal catalysts.

PUBLICATIONS AND PRESENTATIONS

1. "The activities and accomplishments done by LA Tech and GSU JFAP Team", Z. C. Zhong, 2001 JFAP Spring Workshop, Baton Rouge, LA, May 12, 2001.

2. "Nanostructured Particulate Catalytic Materials", B. Tong, Q. Gu, U. Siriwardane, S. V. Naidu, A. N. Murty, and Z. Zhong. Second Louisiana Materials Conference, Baton Rouge, LA, August 25-26, 2001.

3. "Novel Fabrication of Magnetic Oxides", Z.C. Zhong, R.H. Cheng, J. Bosley and P. A. Dowben. Second Louisiana Materials Conference, Baton Rouge, LA, August 25-26, 2001.

4. "Preparation and Characterization of Nanostructured Granular Support and Particles and Catalytic Materials", Z. C. Zhong, S. V. Naidu, A. K. Murty and U. Siriwardane, Annual Meeting on Energy Research and HBCU Project, Pittsburgh, PA, July 26-27, 2001.

5. "Preparation and Characterization of Nano-structured Particulate Catalytic Materials", B. Tong, U. Siriwardane, S. V. Naidu, A. N. Murty, and Z. Zhong. Materials Research Society (MRS) Annual Fall Meeting, Boston, MA, November 25 - December 1, 2001.

6. "Magnetic Oxides prepared by LISD and LCVD", Z. C. Zhong, R. H. Cheng, and P. A. Dowbe, Materials Research Society (MRS) Annual Fall Meeting, Boston, MA, November 25-Decemer 1, 2001.

7. "Annual Report on the Research of Nanostructured Catalytic Materials", Z. C. Zhong Semi-Annual Review Meeting for NSF-EPSCoR, New Orleans, LA, January 25, 2002.

8. "Nanofabrication and Nanostructured Matrials by a novel Laser Chemical Processing", Z. C. Zhong, 2002 APS Annual March Meeting, Indianapolis, IN, March 17-22, 2002.

9. "Magnetization Studies of Cobalt and Iron Deposited Micro-reactors for syngas conversion catalysts", Joann Jones, Keatha Holmes, A.N. Murty, M.F. Ware and S.V. Naidu, Phillip Young Symposium, Grambling, April 2002.

10. "Novel Preparation and Characterization of Nano-structured Catalytic Materials", Z. Zhong, S. V. Naidu, A. N. Murty, U. Siriwardane, Z. Liu and P. Annumwla , DOE-University coal research conference, Pittsburg, PA. June 4-6, 2002.

11. "Magneto-Chemical Character Studies of Alumina Impregnated Cu, Co, Fe, Cu/Co, Cu/Fe and Co/Fe Catalysts for Syngas Conversion", R. Goduguchinta, S.Vudatha, B. G. Barnett, S. N. Vegesna, E. Everett, S. Anderson, R. Besser and

U. Siriwardane, Louisiana Conference on Commercial Applications of Microsystems, Materials and Nanotechnologies, Ruston, Oct. 21-22, 2002.

12. “Synthesis, Chracterization, and Optimization of Alumina Impregnated Cu, Co, Fe, Cu/Co, Cu/Fe and Co/Fe Catalysts for CO Hydrogenation”, S. N. Vegesna, R. Goduguchinta, E. Everett, K. Luurtsema, L. Holeman, A. Emge and U. Siriwardane, Louisiana Conference on Commercial Applications of Microsystems, Materials and Nanotechnologies, Ruston, Oct. 21-22, 2002.

13. “Magnetization and Composition Studies of Co and Fe Encapsulated Al_2O_3 Sol-gel Micro-reactors”, S. V. Naidu, A. N. Murty and M. F. Ware, Micro/Nano Technologies for Advaced Physical & chemical Sensors Consortium, Ruston, Dec. 2002.

14. “Catalytic activity of nano-particle Fe, Co, Co/Fe alumina mesoporus catalysts for CO hydrogenation”, J. Leonard, C.R. Jones, S.V. Naidu, A.N. Murty, S.N. Vegesna, and U.Siriwardane, Louisiana Academy of Science Meeting, Gonzales, LA, March 21, 2003.

15. “Novel SEM and magnetization method to determine pure metal content in Fe_2O_3 nano-particles”, Nwaizugbu, J., S.V. Naidu, A.N. Murty, and U.Siriwardane, Louisiana Academy of Science Meeting, Gonzales, LA, March 21, 2003.

16. “Magnetization and composition studies of Co and Fe encapsulated Al2O3 sol-gel micro-reactors for syngas conversion”, J. Jones, K. Holmes, S.V. Naidu, V.S. Nagineni, S. Zhao, R.K. Aithal, J. Fang, U. Siriwardane, and D. Kuila, Louisiana Academy of Science Meeting, Gonzales, LA, March 21, 2003.

17. "Gas chromatographic analysis of CO and CO_2 hydrogenation using sol-gel prepared Co, Fe, Co/Fe nano-particle catalysts on alumina support", U. Siriwardane, S.V. Naidu, A.N. Murty, S.N. Vegesna, S. Vudatha, B. G. Barnett, S. Anderson, E. Everett, and R. Goduguchinta, 225th American Chemical Society National Meeting, New Orleans, March, 23-27, 203.

18. "Microreactor with sol-gel encapsulated catalysts for syn-gas conversion to higher alkanes", V. S. Nagineni, R. Goduguchinta, S. Zhao, R. K. Aithal, Y. Liang, J. Fang, S.N. Vegesna, U. Siriwardane, S.V. Naidu, J. Palmer, and D. Kuila, 225th American Chemical Society National Meeting, New Orleans, March, 23-27, 2003.

19. “Magneto-Chemical Studies of Co, Fe, and Co/Fe Nano-particles on Sol-gel Prepared Alumina: Hydrogenation of CO/H_2 and CO_2/H_2 Mixtures”, S. V. Naidu, A. N. Murty, J. Leonard and C. Jones, U. Siriwardane, S. N. Vegesna, S. Vudatha, R. Goduguchinta, B. G. Barnett, E. Everett, S. Anderson, K. Luurtsema, L. Holeman, and A. Emge, Materials Research Society Spring Meeting, San Francisco, April 21-25, 2003.

20. “SEM, EDX and Magnetization Studies of Fe and Co Nano-particle Catalysts on Sol-gel Prepared Mesoporus γ-alumina”, S. V. Naidu, U. Siriwardane, A. N. Murty, N. S. Vegesna, J. Nwizugbu, J. Leonard, and C. R. Jones, 7th InterAmerican Congress on Electron Microscopy, San Antonio, TX, Aug. 3-7, 2003. To be publication in Microscopy & Microanalysis, Vol. 9, Supplement 2, 2003.

STUDENTS WORKED ON THE PROJECT

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Novel Preparation and Magneto Chemical Characterization of Nano-Particle Mixed Alcohol Catalysts

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Catalyst Preparation

Preparation of Precursor Sol

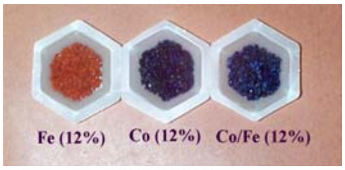
25mL distilled water heated to 75-80 °C
Add 13 mL Aluminum tri-sec-butoxide or 10 g of tri-iso-propoxide
Add 4 mL 1M HNO_3
Reflux for 14 hours

Preparation of sol-gel and gel shaping

Add 5mL 1M HNO_3
Add $Co(NO_3)_2$, $Fe(NO_3)_3$, or $CuNO_3$ solution or nano-particle metal oxides CuO or Fe_2O_3
Drop into mineral oil/ammonia solution. Filled with mineral oil at about 100 °C and one-fourth of cylinder length at the bottom filled with 8-10% NH_3/metal ion solution at room temperature.

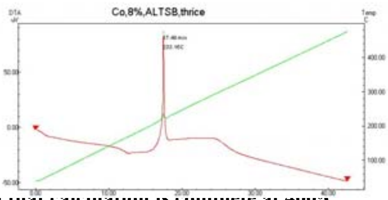
Obtaining Granules:

Filtration followed by washing with cold and alcohol. Then dried at 50 °C for 48 hours. Finally calcined at 450 °C. Tri-iso-propoxide is easier to use, however calcination should be done at slower rate compared to aluminum tri-sec-butoxide to avoid disintegration of granules



DTA Analysis

---Thermogram
---Temperature



DTA data showed that calcination is complete at 400 °C.
- Thermal peaks (~233 °C) assigned to the decomposition of $Co(OH)_2$ to CoO.
- Mixed metals showed several peaks in the range (~230-260 °C).

Hydrogenation of Catalysts

Hydrogenation Cycles

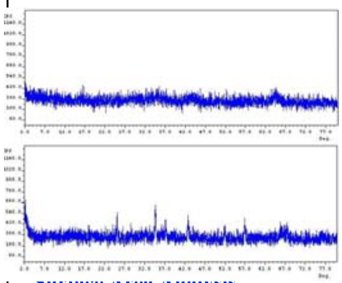
Hydrogen gas passed over the catalyst heated to 400 °C, 2 hrs.
Catalyst dried and water removed by vacuum suction at 400 °C, 1hr
Hydrogen gas passed over the catalyst heated to 400 °C, 2 hrs.
Catalyst dried and by vacuum suction at 400 °C, 1hr.

Catalysts granules could be made either by aluminum tri-sec-butoxide or tri-iso-propoxide. Latter is easy to use but needed a slower calcination step to maintain comparable granular characteristics. Sol-gel procedure was modified to prepare granules using Sol-gel and nano-metal oxide.

Catalyst Characterization

PXRD Analysis: 12% Fe on Alumina Supported Catalyst

The metal oxide peaks are prominent in sample annealed at 450 °C (bottom).



PXRD showed broad peaks of alumina and almost no peaks for metal oxides until the compositions were over 12%.

Weak peaks for metal oxides indicate lack of regular lattice spacing and/or smaller particle size of metal oxide particles.

PXRD data supports that metal oxide particles are in the nano-particle range.

Surface Area Analysis

Metal	Composition	Surface Area
Co(%)w/w	4	350
Fe(%)w/w	4	310
Co/Fe(%)w/w	2:2(4)	351
Surface area is basesd on N2 desorption		
m2/g. Nova 3000		

Brunauer-Emmett-Teller (BET) method is using N_2 desorption.

Surface area of the catalysts were high in the range 250-350 m²/g.

Pore structures are in the mesoporous range.

EDX Analysis: Metal Loading

Metal	Composition	EDX %
Co(%)w/w	4	20
Fe(%)w/w	4	140
Co/Fe(%)w/w	2:2(4)	30:29(59)
EDX Energy Dispersive X-ray Analysis		

Specific metal loading, as determined by EDX, is reproducible.

Increasing metal concentration in the bottom aqueous ammonia solution increase the metal loading.

In Co/ Fe mixtures Co interferes and reduces the Fe metal loading, which could be due higher solubility of Co metal hydroxides formed during sol-gel preparation.

Sol-gel and metal solution prepared granules contain nano-particle metal catalysts. Sol-gel and nano-metal oxide prepared granules have similar characteristics. Nano-particle metal oxide method yields higher metal loading.

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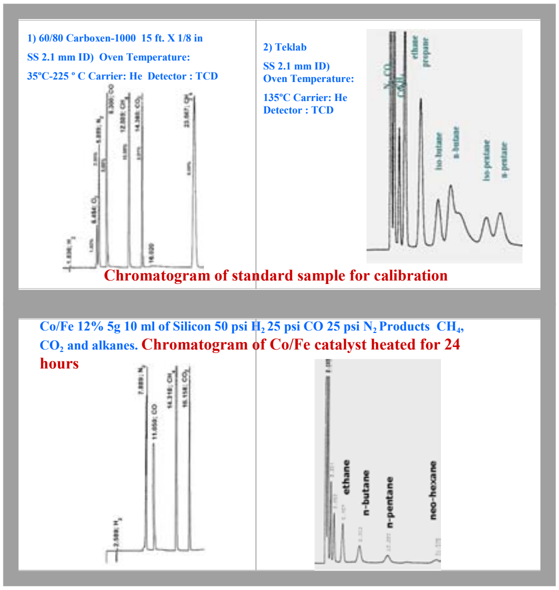
Catalytic Activity

GC Analysis of (non-polar) Gases



CO conversion data for catalysts prepared by sol-gel solution method

Metal Composition	Catalytic activity
Cu	39%
Co	55%
Fe	48%
Cu/Co	43%
Co/Fe	79%
Cu/Fe	41%

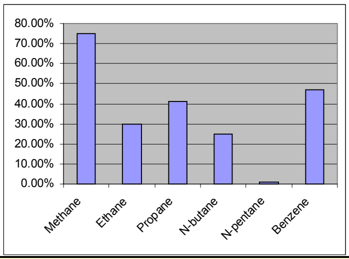
Comparison CO conversion by catalysts prepared by sol-gel and co-precipitation methods

Metal	Sol-gel	Co-precipitation
Co	55%	44%
Fe	48%	42%
Co/Fe	79%	60%

Comparison CO conversion by catalysts prepared by sol-gel method starting from metal solution and nano-metal oxide.

Metal	Metal Solution	Nano-metal oxide
Cu	39%	43%
Fe	48%	52%
Cu/Fe	41%	47%

Alkane Composition of Catalytic Mixtures CO/H_2: 2:3

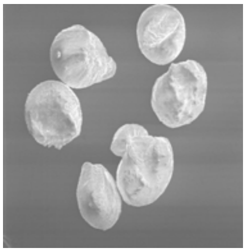


- Catalyst with mixed metal Fe/Co(6%/6%) compositions at total 12% (prepared by sol-gel and metal solutions 12% showed the best conversion rates for the syngas ($CO+H_2$).
- Nano-particle catalysts on sol-gel prepared meosporus γ-alumina showed higher conversion rates compared to conventional catalysts prepared by co-precipitation methods.
- Catalyst with mixed metal Fe/Co(6%/6%) compositions at total 12% (prepared by sol-gel and nano-particle metal oxide 12% showed slightly higher or comparable conversion rates for the syngas ($CO+H_2$) compared to sol-gel and metal solutions prepared catalysts.
- The amount of higher alkanes increased with increasing CO/H_2 ratio: 1:2, 2:3 and 1:1.

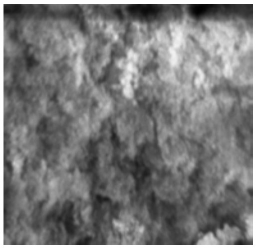
Granular and Magnetic Characteristics

Granular Characteristics

SEM of γ-alumina granules at 50 X. Average granule size ~1 mm.

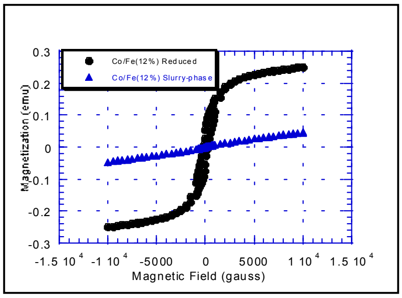


SEM of granular surface at 60,000 X showing porous structure and 50 nm particles.



Magnetic Characteristics

Magnetization of Fe/Co (12%) catalysts: ● Reduced ▲ After slurry-phase reaction.



Energy Depressive X-ray Analysis and Magnetization Results

Sample	Description	σ (emu/g) (VSM)	Fe % (EDX)	Co % (EDX)	Pure Metal %
Pure Co					
Co(12%)	Reduced	5.94	0	3.9	94.35
Co(12%)	After reaction (gas-phase)	4.40	0	3.9	69.84
Co(12%)	After reaction (slurry-phase)	2.46	0	3.9	39.05
Pure Fe					
Fe(12%)	Reduced	0.71	2.1	0	15.57
Fe(12%)	After reaction (gas-phase)	0.05	2.1	0	1.11
Fe(12%)	After reaction (slurry-phase)	0.04	2.1	0	0.81
Mixed Metal					
Fe/Co(12%)	Reduced	1.81	2.9	7.6	9.75
Fe/Co(12%)	After reaction (gas-phase)	1.56	2.9	7.6	8.41
Fe/Co(12%)	After reaction (slurry-phase)	0.05	2.9	7.6	0.28

Conclusions

- The nano-particle nature of catalyst and support was confirmed by SEM and X-ray diffraction indicating a higher porous structure and its mesoporus nature.
- Catalyst with mixed metal Fe/Co compositions at 12% (prepared by sol-gel/oil- drop and metal solutions 12% showed the best conversion rates for the syngas ($CO+H_2$).
- Nano-particle catalysts on sol-gel prepared meosporus γ-alumina showed higher conversion rates compared to conventional catalysts prepared by co-precipitation methods.
- Magnetization studies of post-reaction Co and Fe nano-catalysts showed that the formation of carbides is higher Fe compared to Co.

Acknowledgments

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